

Chapter 52 – SANS FROM POLYMER BLENDS UNDER PRESSURE

1. INTRODUCTION

Pressure is another parameter relevant to the understanding of the phase separation and thermodynamic behavior of polymer blends. Polymer blend mixtures phase separate either upon cooling and are characterized by an Upper Critical Spinodal Temperature (UCST) behavior or upon heating in which case they are characterized by a Lower Critical Spinodal Temperature (LCST) behavior. The UCST behavior is driven by enthalpic interactions between monomers whereas it is argued that the LCST behavior is due to “free volume”. Free volume is related to the packing ability of monomers and is related to many factors among which polymer chemistry (side group bulkiness).

The mean field Flory-Huggins theory is a broadly used model that describes polymer blend miscibility. The chi parameter has two main contributions, one entropic and one enthalpic in nature. This theory is the basis for the Random Phase Approximation (RPA) approach used to model the scattering from homogeneous polymer blends. The commonly used RPA equations assume incompressible blends. Extension of the RPA equations to describe compressible blends will be discussed.

The goal here is to investigate the effect of hydrostatic pressure on the UCST and LCST phase behaviors and to account for equation-of-state (i.e., compressibility) effects using the SANS technique with in-situ pressure. Pressure can be controlled faster than temperature and is therefore more effective for thermodynamic studies. Pressure is also an important factor in polymer processing.

The in-situ pressure cell consists mainly of two sapphire windows separated by a fixed gap (typically 1 mm) in which a polymer wafer is confined inside an o-ring. Pressure is applied to the sample through the o-ring so that the pressurizing fluid never gets in contact with the sample. In-situ pressure can be varied typically up to a couple of kilobars (note that 1 bar = 1 atm = 760 mm Hg = 14.7 psi = 100 kPa) and temperature can be varied up to 160 °C. This gives a wide window in parameter space.

2. THE DPS/PVME POLYMER BLEND UNDER PRESSURE

SANS with in-situ pressure has been applied to a series of deuterated polystyrene (dPS) and polyvinyl methyl ether (PVME) blends with various compositions (Hammouda-Bauer, 1995). Molecular weights were $M_w = 188,000$ g/mol ($M_w/M_n = 1.02$) for dPS and $M_w = 201,000$ g/mol ($M_w/M_n = 1.49$) for PVME. The dPS volume fractions in dPS/PVME were chosen as 10 %, 30 % and 50 % respectively. It is known that the dPS/PVME blend is characterized by an LCST behavior with a minimum (critical point) at around 20 % dPS. The effect of pressure is to raise the LCST line since its effect is to damp out composition fluctuations. This is manifested as a lowering of the scattering intensity. In order to monitor composition fluctuations, the forward scattering intensity

$I(0)$ is obtained using a Zimm plot (plot of $I^{-1}(Q)$ vs Q^2). It was found that pressure favors mixing for the dPS/PVME blend in most cases.

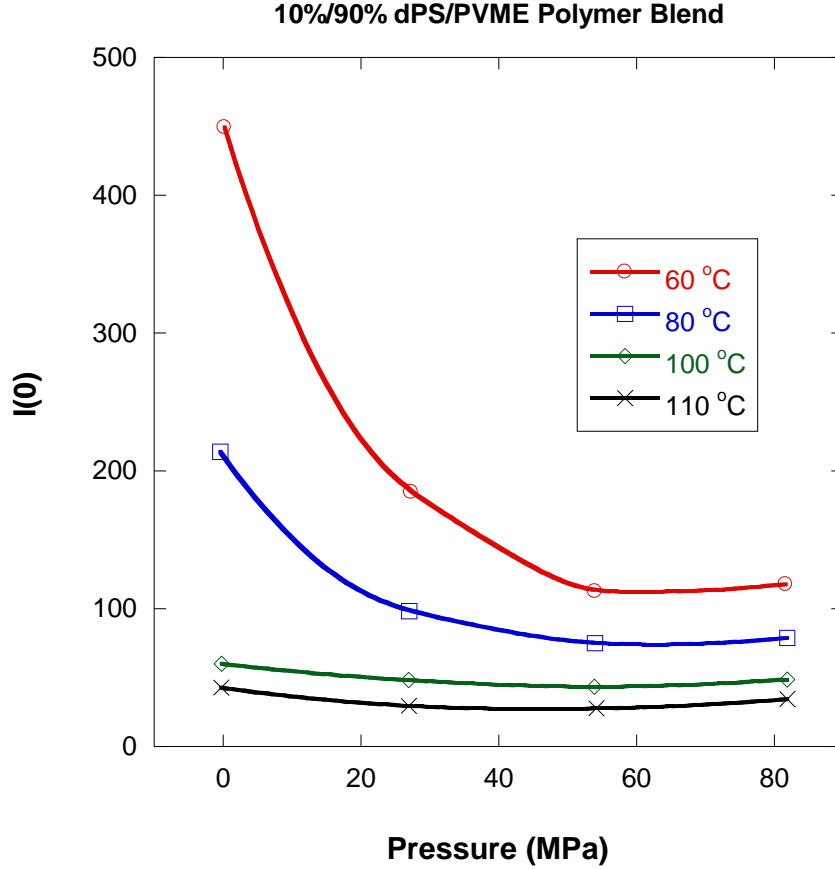


Figure 1: Variation of the forward scattering intensity $I(0)$ with pressure for the 10 %/90 % dPS/PVME sample at various temperatures. A line through the points is included as a guide to the eye.

A pressure-induced increase of the spinodal line with pressure (evidenced by a decrease of the scattering intensity $I(0)$) of as much as 30 °C/kbar was observed.

Since pressure can be changed fast, spinodal decomposition can be controlled at will even for this strongly interacting blend. Following pressure change strategies, one could get in and out of the spinodal phase demixing region. This is observed as the formation of a spinodal ring which quickly disappears under the beamstop.

As a first step in understanding the SANS data, recall the incompressible RPA equation for polymer blends:

$$\frac{(\rho_1 - \rho_2)^2}{d\Sigma(Q)/d\Omega} = \frac{1}{n_1\phi_1v_1P_1(Q)} + \frac{1}{n_2\phi_2v_2P_2(Q)} - \frac{2\chi_{12}}{v_0}. \quad (1)$$

Here, the standard notation has been used for the degrees of polymerization (n_1 and n_2), volume fractions ϕ_1 and ϕ_2 , monomer volumes v_1 and v_2 , Debye functions $P_1(Q)$ and $P_2(Q)$, scattering length densities ρ_1 and ρ_2 and chi parameter χ_{12}/v_0 .

The Flory-Huggins interaction parameter has two contributions: one entropic and one enthalpic in nature, $\chi_{12} = C + \frac{D}{T}$. Our measurements showed that both contributions increase with pressure. This interaction parameter is characterized by a composition-dependence. Our measurements also showed that this dependence is not due to compressibility effects.

The form factors can be expanded at low- Q as $\frac{1}{P_1(Q)} = 1 + \frac{Q^2 R_{g1}^2}{3}$. This changes the incompressible RPA equation to the low- Q expansion as:

$$\frac{(\rho_1 - \rho_2)^2}{d\Sigma(Q)/d\Omega} = \frac{1}{n_1\phi_1v_1} + \frac{1}{n_2\phi_2v_2} - \frac{2\chi_{12}}{v_0} + \left(\frac{1}{n_1\phi_1v_1} \frac{R_{g1}^2}{3} + \frac{1}{n_2\phi_2v_2} \frac{R_{g2}^2}{3} \right) Q^2. \quad (2)$$

The Zimm plot slope B in $\Gamma^{-1}(Q) = \Gamma^{-1}(0) + BQ^2$ is proportional to the radii of gyration.

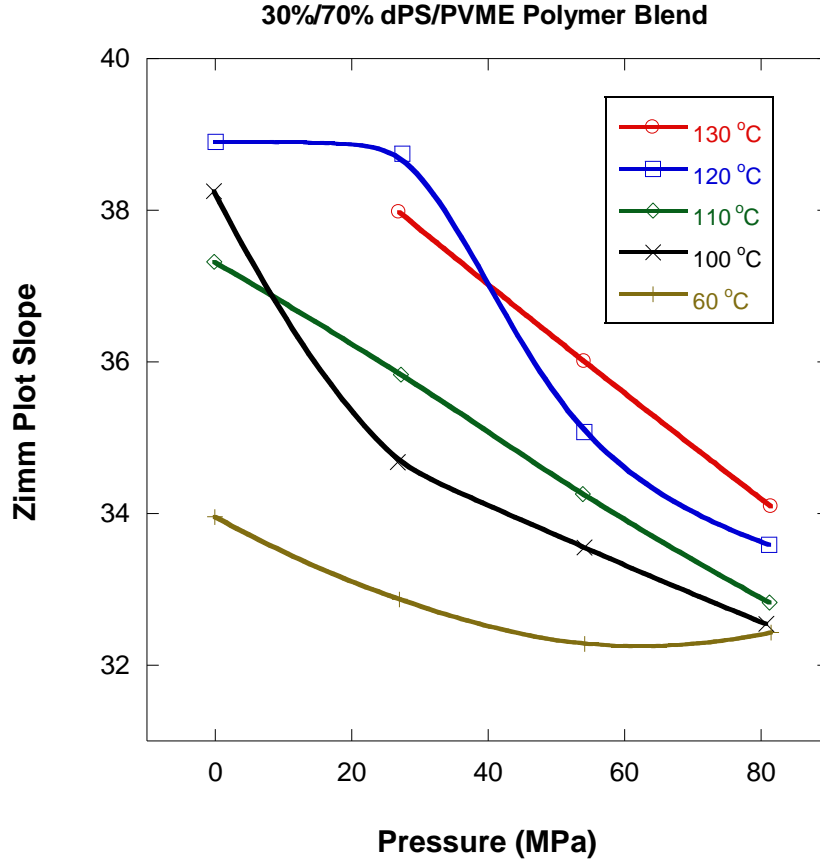


Figure 2: Variation of the Zimm plot slope B (obtained from $I^{-1}(Q) = I^{-1}(0) + BQ^2$) with pressure for the 30 %/70 % dPS/PVME sample measured at various temperatures.

This Zimm plot slope is seen to decrease with pressure. There is no reason for pressure to affect the radii of gyration. This artifact is due to the incompressible assumption in the RPA model. A compressible RPA model is described next.

3. COMPRESSIBLE POLYMER BLEND MODEL

In order to include compressibility effects, an equation-of-state is used. It describes density variation with temperature and pressure (using so-called PVT measurements). Various equation-of-state models are available to describe free volume effects in polymers (1) cell models associate a free volume component as part of the monomer volume, (2) lattice-fluid models assume free volume as a separate component, and (3) hole models assume a combination of the above two features. Here a simple lattice-fluid model is used (Sanchez-Bidkar, 1995).

Consider the “mixing” polymer volume fractions for the two polymer components ϕ_1 and ϕ_2 defined previously such that $\phi_1 + \phi_2 = 1$. Introduce a free volume fraction f_0 and new fractions $f_1 = \phi_1(1-f_0)$ and $f_2 = \phi_2(1-f_0)$ such that $f_1 + f_2 + f_0 = 1$. f_0 is not directly measurable

but can be estimated through PVT (density) measurements. Define monomer “hard-core” volumes v_1^* and v_2^* , the statistical segment lengths a_1 and a_2 , neutron scattering length densities ρ_1 and ρ_2 and degrees of polymerization n_1 and n_2 .

The lattice-fluid equation-of-state uses a characteristic energy density (internal pressure) P^* and characteristic temperature T^* for each of the components. These are tabulated quantities for each polymer. The **lattice-fluid equation-of-state** reads:

$$(1 - f_0)^2 + \frac{P}{P^*} + [\ln(f_0) + 1 - f_0] \frac{T}{T^*} = 0. \quad (3)$$

The term $\frac{1}{n} = \frac{\phi_1}{n_1} + \frac{\phi_2}{n_2}$ appearing in the original model has been neglected for typical (large) degree of polymerization ($n \gg 1$).

Mixing rules are used to connect the two polymer components:

$$P^* = \phi_1^2 P_1^* + 2\phi_1\phi_2 P_{12}^* + \phi_2^2 P_2^* \quad (4)$$

$$\frac{P^*}{k_B T^*} = \frac{1}{v_0} = \frac{\phi_1 P_1^*}{k_B T_1^*} + \frac{\phi_2 P_2^*}{k_B T_2^*}.$$

These equations describe the compressibility part of the blend mixture.

The compressible binary mixture can be assumed to be a ternary incompressible mixture where the third component consists of “holes” (think free volume). The Gibbs free energy density for this ternary mixture (polymers 1 and 2 and holes as the third component) has the usual entropic part (three terms) and the entropic part (3 binary interactions). The scattering intensity is obtained using a **three component RPA approach**. The **ternary RPA equations** have been discussed previously. They are repeated here for convenience. The SANS cross section is given by the following set of equations (Hammouda-Benmouna, 1995):

$$\frac{d\Sigma(Q)}{d\Omega} = \rho_1^2 S_{11}(Q) + \rho_2^2 S_{22}(Q) + 2\rho_1\rho_2 S_{12}(Q). \quad (5)$$

$$S_{11}(Q) = \frac{S_{11}^0(Q)(1 + v_{22}S_{22}^0(Q))}{(1 + v_{11}S_{11}^0(Q))(1 + v_{22}S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q)S_{22}^0(Q)}$$

$$S_{22}(Q) = \frac{S_{22}^0(Q)(1 + v_{11}S_{11}^0(Q))}{(1 + v_{11}S_{11}^0(Q))(1 + v_{22}S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q)S_{22}^0(Q)}$$

$$S_{12}(Q) = \frac{-S_{11}^0(Q)v_{12}S_{22}^0(Q)}{(1 + v_{11}S_{11}^0(Q))(1 + v_{22}S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q)S_{22}^0(Q)}$$

$$\begin{aligned}
S_{11}^0(Q) &= n_1 f_1 v_1^* P_1(Q) \\
S_{22}^0(Q) &= n_2 f_2 v_2^* P_2(Q) \\
S_{00}^0 &= f_0 v_0
\end{aligned}$$

$$v_{11} = \frac{1}{S_{00}^0} - 2 \frac{P_1^*}{k_B T} + C_{11}$$

$$v_{22} = \frac{1}{S_{00}^0} - 2 \frac{P_2^*}{k_B T} + C_{22}$$

$$v_{12} = \frac{1}{S_{00}^0} - 2 \frac{P_{12}^*}{k_B T} + C_{12}$$

$$C_{11} = -2\phi_2 \frac{[\ln(f_0) + (1-f_0)]}{(1-f_0)^2} \left(\frac{P_1^*}{k_B T_1^*} - \frac{P_2^*}{k_B T_2^*} \right)$$

$$C_{22} = 2\phi_1 \frac{[\ln(f_0) + (1-f_0)]}{(1-f_0)^2} \left(\frac{P_1^*}{k_B T_1^*} - \frac{P_2^*}{k_B T_2^*} \right)$$

$$C_{12} = (\phi_1 - \phi_2) \frac{[\ln(f_0) + (1-f_0)]}{(1-f_0)^2} \left(\frac{P_1^*}{k_B T_1^*} - \frac{P_2^*}{k_B T_2^*} \right).$$

This formalism is tied up using the following **bridging relation** between the energy densities P_{ij}^* and the monomer-monomer interaction parameters W_{ij} :

$$P_{ij}^* = -\frac{W_{ij}}{2v^*}. \quad (6)$$

Here $v^* = \sqrt{v_1^* v_2^*}$ is a reference volume and $P_{11}^* = P_1^*$ is understood.

The lattice-fluid equation-of-state and the compressible RPA equations are solved self-consistently (i.e., iteratively till convergence is obtained). The iterative process is carried out using an **initial guess**: $P_{12}^* = \sqrt{P_1^* P_2^*}$.

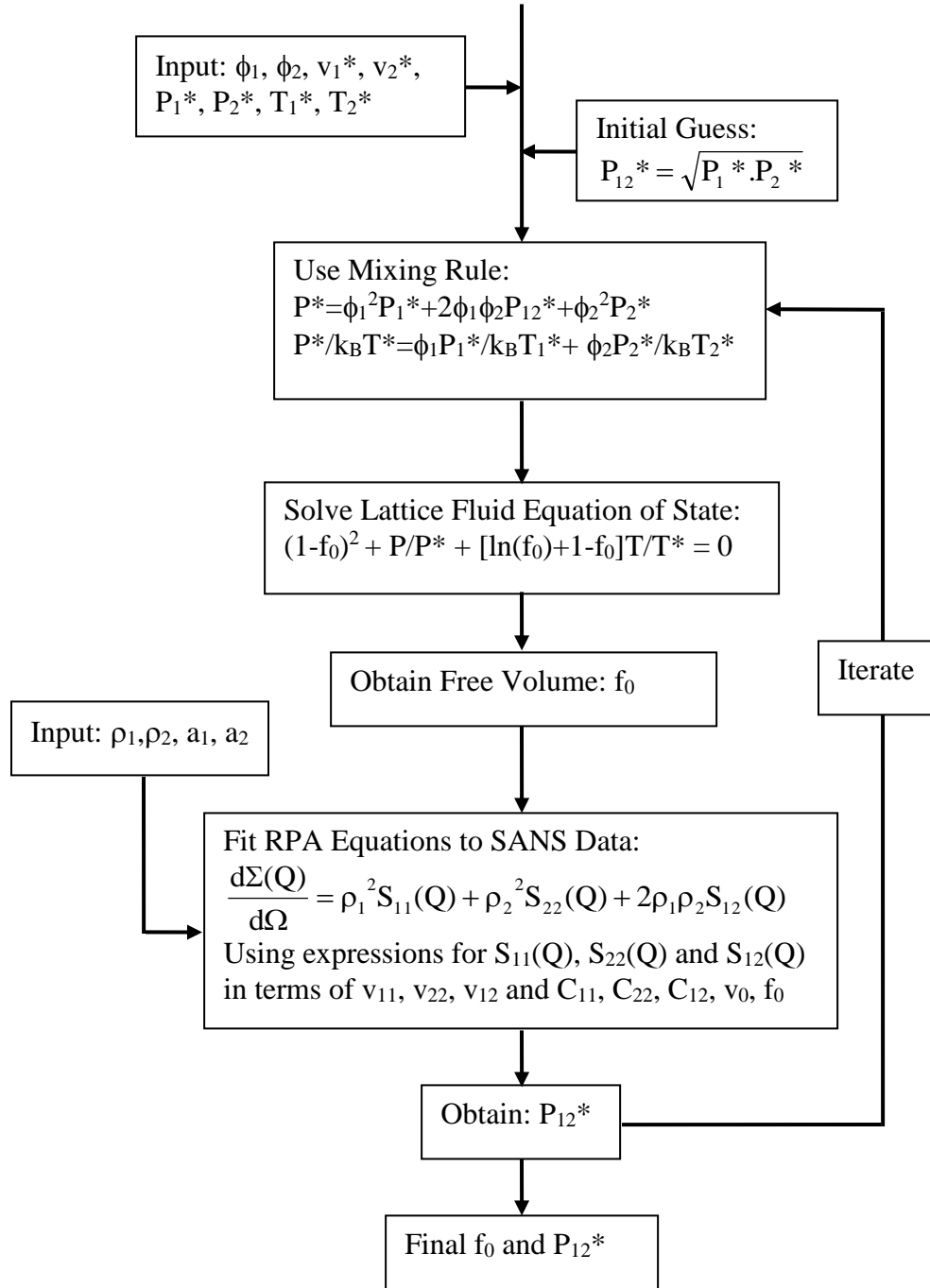


Figure 3: **Self-consistent approach** to calculate the scattering intensity for compressible polymer blends using the lattice-fluid equation-of-state and the compressible RPA equations.

This formalism is applied here to the dPS/PVME blend under pressure. Tabulated values for dPS are $P_1^* = 355$ MPa and $T_1^* = 731$ K and for PVME they are $P_2^* = 353$ MPa and

$T_2^* = 657$ K. Some results for the free volume fraction for increasing temperature and pressure follow.

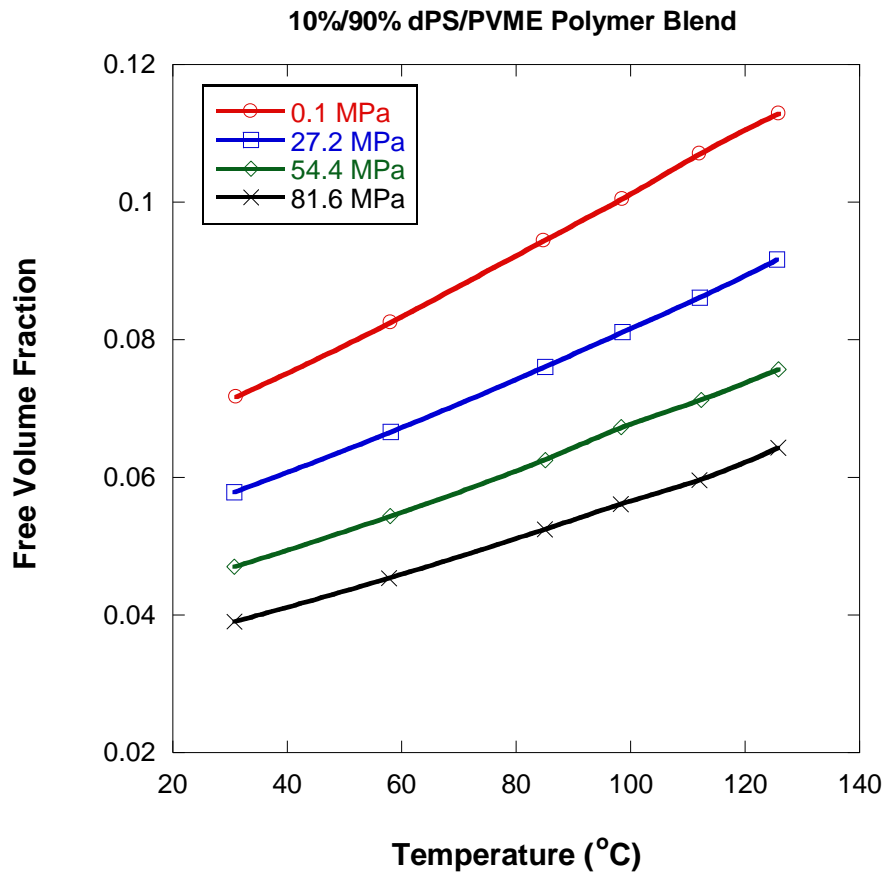


Figure 4: Variation of the free volume fraction f_0 for increasing temperature for the 10 %/90 % dPS/PVME polymer blend.

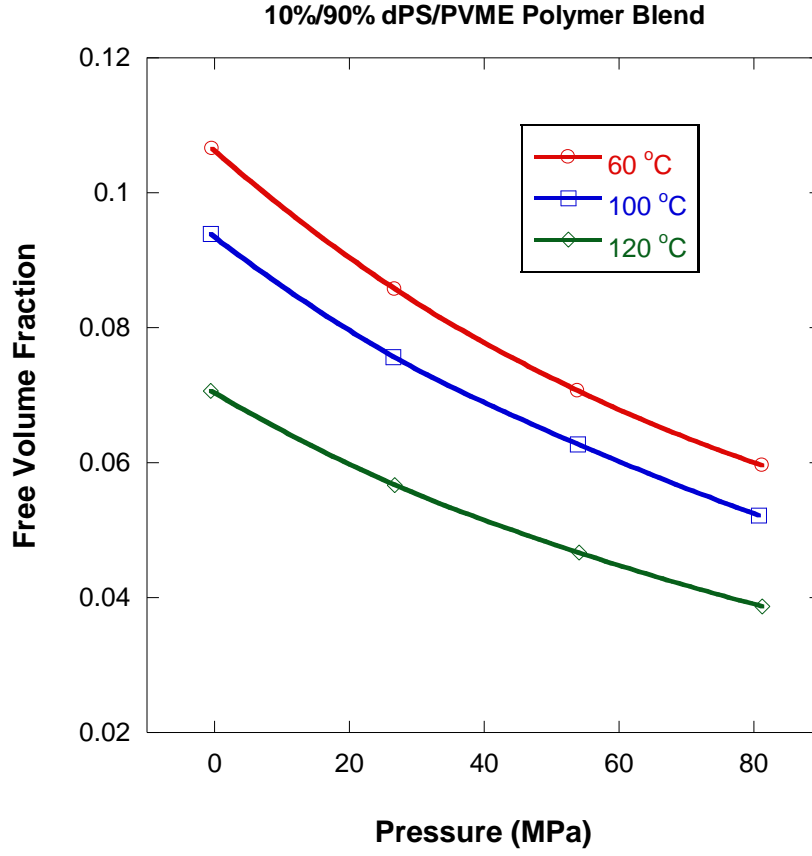


Figure 5: Variation of the free volume fraction f_0 for increasing pressure for the 10 %/90 % dPS/PVME polymer blend.

The free volume fraction f_0 is seen to increase with temperature and decrease with pressure as it should.

The inter-monomer interaction energy density P_{12}^* is plotted next with and without free volume (i.e., with $f_0 = 0$). This variation is seen to have weak variation for increasing pressure and to decrease consistently with increasing temperature. These results are reasonable since increasing temperature moves the blend closer to phase separation.

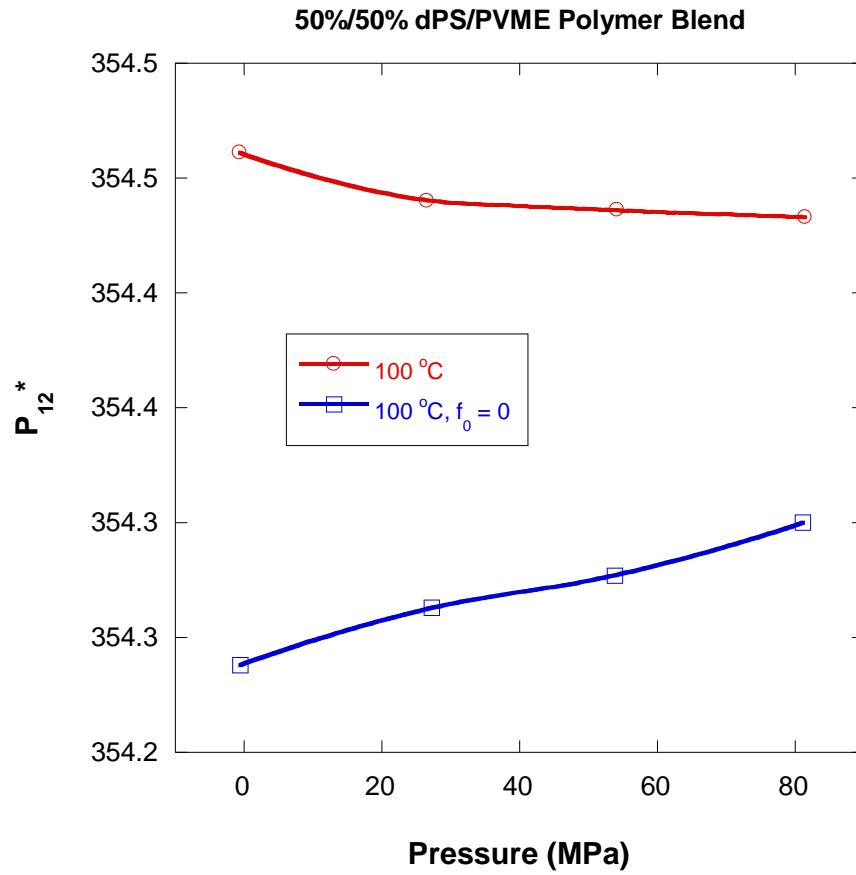


Figure 6: Variation of the inter-component interaction energy density P_{12}^* for increasing pressure for the 50 %/50 % dPS/PVME.

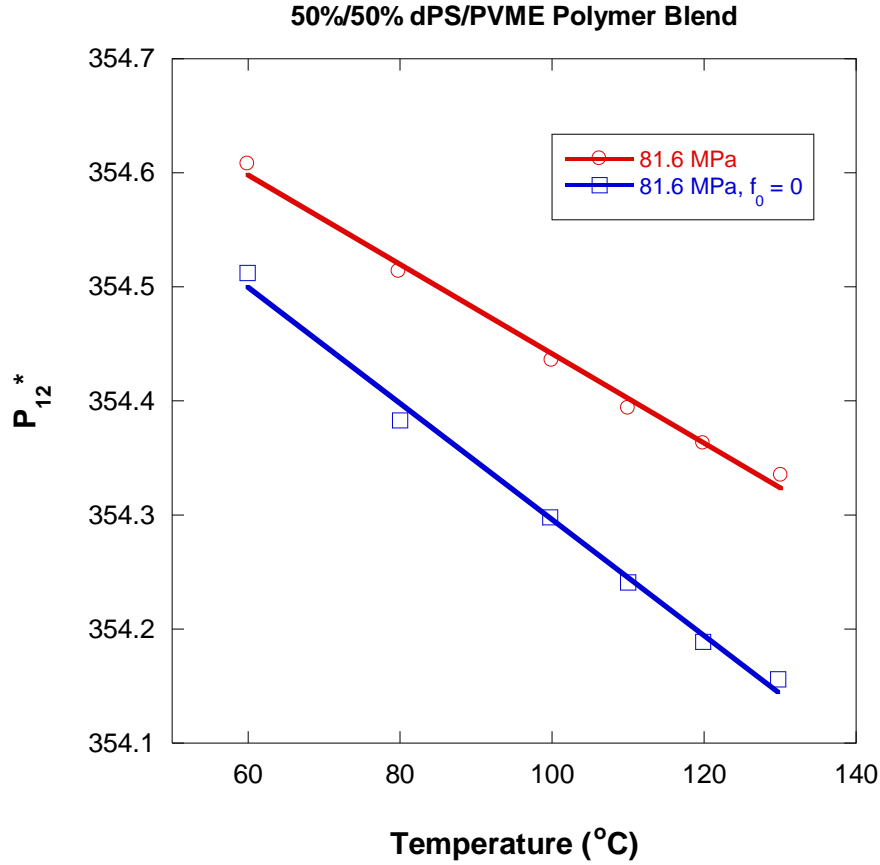


Figure 7: Variation of the inter-component interaction energy density P_{12}^* for increasing temperature for the 50 %/50 % dPS/PVME.

The compressible RPA model used here to fit the SANS data is highly nonlinear and yields wide variations in intensity for slight variation in interaction energy density P_{12}^* . P_{12}^* was found to depend on pressure (weakly) and on temperature (linearly).

4. A POLYOLEFIN POLYMER BLEND UNDER PRESSURE

Model polyolefins of molecular weight around 200,000 g/mol consisting of deuterated polymethyl butylene (dPMB) and polyethyl butylene (PEB) were blended and investigated under pressure. A PMB-PEB diblock copolymer was added in order to adjust the phase diagram to a convenient temperature range. The degrees of polymerization were 4260 for dPMB, 3350 for PEB and 3740 for the PMB-PEB diblock. The relative fraction of PEB monomers in the PMB-PEB diblock was 0.33. The dPMB/PEB relative volume fraction was also 0.33.

The SANS technique was used with in-situ pressure in order to investigate the effect of pressure on the spinodal and binodal temperatures for this polyolefin blend (Hammouda et al, 1997). The spinodal temperature T_s is obtained from an extrapolation of the plot of $I^{-1}(0)$ vs T^{-1} where $I(0)$ is the forward scattering intensity obtained from a Zimm plot and

T is the absolute temperature (in K). The binodal temperature T_b on the other hand is obtained when $I^1(0)$ becomes negative. Note that the region between T_b and T_s is the nucleation and growth region. When pressure is increased, both T_s and T_b are seen to increase. In other words, pressure favors phase separation (demixing).

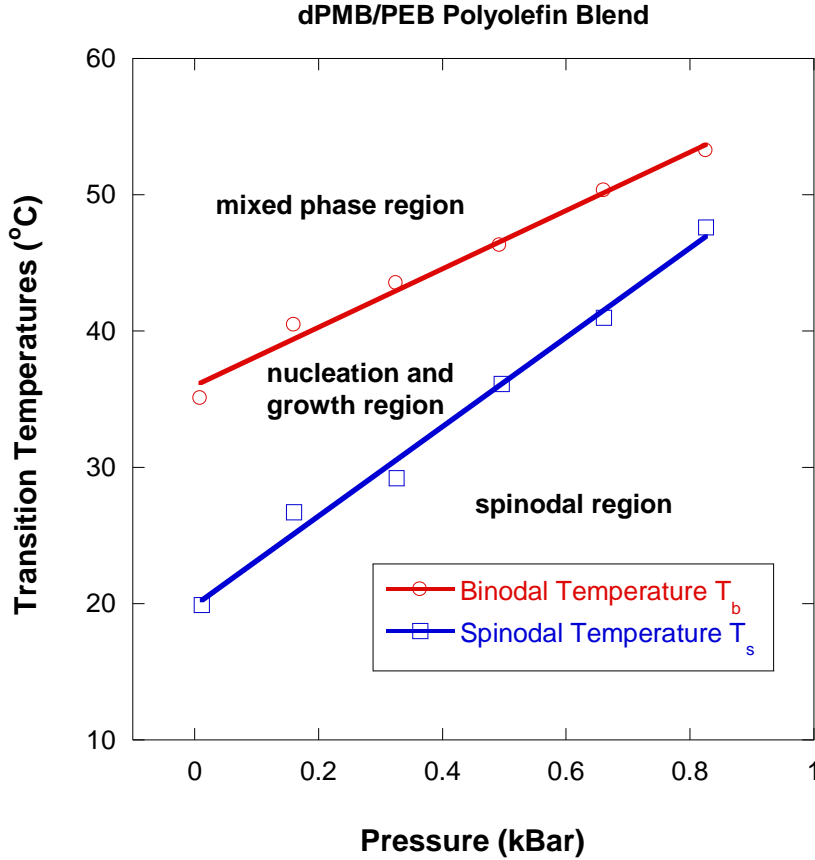


Figure 8: Variation of the binodal and spinodal transition temperatures with pressure for the dPMB/PEB polyolefin blend. The nucleation and growth and the spinodal regions constitute the so-called phase separation region.

A simple description of compressibility effects through a pressure-dependent Flory-Huggins interaction parameter $\chi_{12} = E + FP$ showed that E (related to the internal energy change ΔU upon mixing) and F (related to the volume change ΔV upon mixing) are proportional. This means that the volume increase upon mixing is a linear response of the repulsive interactions between monomers (Lefebvre et al, 1999).

Here also, varying pressure gives a fast-response way for moving from the mixed phase region to the phase separated region of the phase diagram. This allows the monitoring of the phase separation kinetics during phase separation. The reverse phase-mixing kinetics have also been investigated (Hammouda et al, 1997).

5. THE DPS/PBMA POLYMER BLEND UNDER PRESSURE

Another polymer blend was investigated using in-situ pressure. It consisted of dPS blended with poly-n-butyl methacrylate noted PBMA for short (Hammouda-Bauer, 1995). The molecular weights were $M_w = 10,000$ g/mol ($M_w/M_n = 1.03$) for dPS and $M_w = 34,000$ g/mol ($M_w/M_n = 1.96$) for PBMA. This blend is characterized by a miscibility gap. In-situ pressure affects both the UCST and the LCST branches of the phase diagram. This is seen as a systematic decrease of the scattering intensity for all temperatures. Here also, pressure dampens composition fluctuations and widens the miscibility gap.

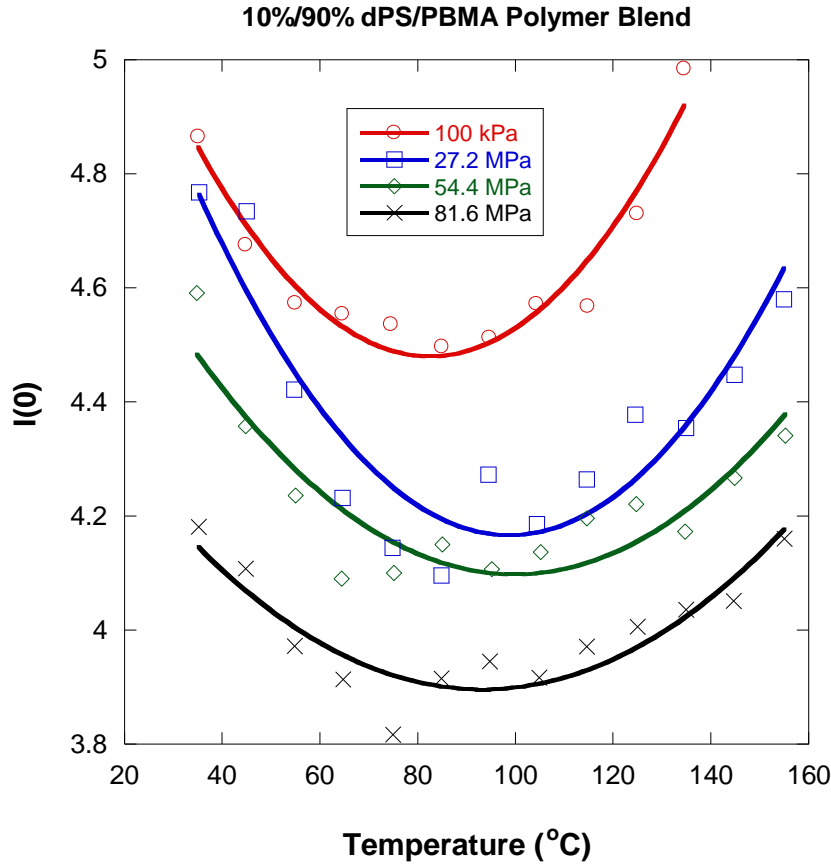


Figure 9: Variation of the forward scattered intensity $I(0)$ with temperature for the 10%/90% dPS/PBMA sample for various pressures. The upturn variation is characteristic of a miscibility gap. The lines are parabolic fits included to better visualize the trends.

Pressure seems to affect the high temperature branch (LCST) more than the low temperature branch (UCST). It also shifts the miscibility gap to a slightly higher temperature.

6. SUMMARY AND DISCUSSION

Pressure affects both the UCST and the LCST branches of the phase diagram in polymer blends. Based on the blends considered here, a few conclusions can be summarized.

Pressure can raise the LCST which is driven by free volume. It can either raise or lower the UCST (driven by monomer-monomer interactions). It should be noted that in other instances (not described here), pressure can lower the LCST such as in the case of solutions of poly(ethylene oxide) in deuterated water (PEO/d-water). In that case, the LCST is driven by specific interactions (hydrogen bonding) that soften under pressure. These points are summarized elsewhere (Hammouda, 2001).

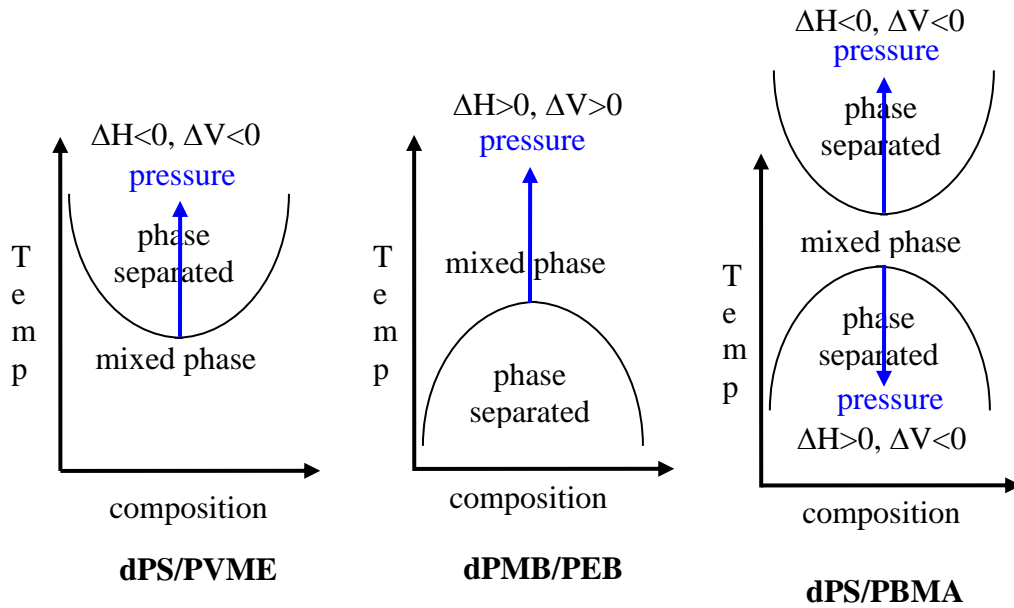


Figure 10: Pressure effects on the thermodynamics of phase-mixing for three polymer blends.

The phase separation lines can either increase or decrease with pressure. This can be understood in terms of the Clausius-Clapeyron equation:

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta H}. \quad (7)$$

Here dT/dP is the derivative of the temperature variation with pressure along the phase separation curve and ΔV and ΔH are the volume change and enthalpy change upon phase-mixing. For a UCST system, mixing happens upon heating ($\Delta H > 0$). If the volume change upon mixing is positive $\Delta V > 0$, then pressure increases the UCST line (as in the case of dPMB/PEB). If on the other hand $\Delta V < 0$, then pressure decreases the UCST line (as in the case of dPS/PBMA). For an LCST system, mixing happens upon cooling ($\Delta H < 0$).

Similarly, if $\Delta V < 0$ then $dP/dT > 0$ and pressure increases the LCST line (as in the cases of dPS/PVME and dPS/PBMA). This is the case of LCST driven by free volume (which decreases upon cooling). If on the other hand $\Delta V > 0$, then $dP/dT < 0$ and pressure decreases the LCST line as in the case of PEO/d-water (not shown here). This is the case of LCST due to hydrogen bonding (which causes the volume to increase upon cooling).

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QUESTIONS

1. How is pressure applied to the sample in an in-situ pressure cell?
2. Describe the LCST and UCST phase behaviors.
3. Describe a miscibility gap.
4. What is meant by "free volume" in polymer blends? What causes free volume?
5. What is the effect of pressure on an LCST system driven by free volume?
6. Does the UCST line increase or decrease with increasing pressure? Why?
7. What is an equation-of-state? Name an equation-of-state used for polymers.
8. State the Clausius-Clapeyron equation. Define the various terms.

ANSWERS

1. The in-situ pressure cell uses an o-ring confined between two sapphire windows. The sample itself is melt-pressed into the right volume and confined in the o-ring. The pressurizing fluid compresses the o-ring thereby pressurizing the sample.
2. Phase separation occurs through heating in a Lower Critical Spinodal Temperature (LCST) system whereas it occurs through cooling in a UCST system.
3. Phase separation occurs both through heating and cooling when a polymer blend is characterized by a miscibility gap with an LCST at high temperature and a UCST at low temperature.
4. Free volume means the less-than-perfect packing of monomers in the blend. Free volume decreases during densification. Free volume can be caused by bulky side groups that are hard to pack tightly.
5. Free volume is squeezed out when pressure is applied. This raises the LCST with increasing pressure.
6. The UCST could either increase or decrease with increasing pressure. This is due to the possibility of a positive or negative volume change upon mixing in blends.
7. An equation-of-state describes the variation of density with temperature and pressure. The lattice-fluid equation-of-state is used to describe polymers.
8. The Clausius-Clapeyron equation is stated as: $\frac{dT}{dP} = \frac{\Delta V}{\Delta H}$ where dT/dP is the derivative of the temperature variation with pressure along the phase separation curve and ΔV and ΔH are the volume change and enthalpy change upon phase-mixing.